

Synthesis of novel alkoxyated triacylglycerols and their lubricant base oil properties[☆]

A. Adhvaryu^{a,b}, Z. Liu^b, S.Z. Erhan^{b,*}

^a Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802, USA

^b USDA/NCAUR/ARS, Food and Industrial Oil Research, 1815 N. University Street, Peoria IL 61604, USA

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Abstract

Development and application of bio-based fluids in industrial and automotive sectors are rapidly increasing due to their non-toxic and biodegradable character unlike mineral oil-based products. Synthetic lubricant base fluid with improved high and low-temperature stability was prepared by chemical modification of epoxidized soybean oil (ESBO). The reaction was carried out in two-steps: (i) synthesis of dihydroxylated soybean oil from ESBO with HClO_4 , (ii) reaction of acetic, butyric and hexanoic anhydride with the dihydroxylated product. The composition of the reaction products were confirmed by NMR and FTIR analysis. Chain length variation of the anhydrides used in the synthesis resulted in base fluids with different physical and chemical properties. Low-temperature stability was excellent for hexanoic anhydride derivative. When compared with SBO, thermal and oxidative stabilities were improved. Viscosity, volatility and other lubricant base oil properties were evaluated qualitatively. Bio-fluids based on this chemical modification offer great potential for the development of industrial fluids and products based on such fluids.

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Keywords: Vegetable oils; Epoxidized soybean oil; Dihydroxylation; Alkoxyated triacylglycerol; Oxidation; Pour point

1. Introduction

During the last decade due to strict government and environmental regulations, there has been a constant demand for environmentally friendly lubricants (Rhee,

1996). Most of the lubricants originate from petroleum stock, which is toxic to environment and difficult to dispose. Vegetable oils with high oleic content are considered to be potential candidates to substitute conventional mineral oil-based lubricating oils and synthetic esters (Randles and Wright, 1992; Asadauskas et al., 1996). Vegetable oils are preferred over synthetic fluids because they are renewable resources and cheaper.

Vegetable oils as lubricants are preferred because they are biodegradable and non-toxic, unlike conventional mineral-based oils (Randles and Wright, 1992; Battersby et al., 1998). They have very low volatility due to the high molecular weight of the triacylglycerol

[☆] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

* Corresponding author. Tel.: +1-309-681-6532;
fax: +1-309-681-6340.

E-mail address: erhansz@ncaur.usda.gov (S.Z. Erhan).

molecule and have a narrow range of viscosity changes with temperature. Polar ester groups are able to adhere to metal surfaces, and therefore, possess good boundary lubrication properties. In addition, vegetable oils have high solubilizing power for polar contaminants and additive molecules.

On the other hand, vegetable oils have poor oxidative stability (Gapinski et al., 1994; Becker and Knorr, 1996) primarily due to the presence of bis allylic protons and are highly susceptible to radical attack and subsequently undergo oxidative degradation to form polar oxy compounds. This phenomena result in insoluble deposits and increases in oil acidity and viscosity. Vegetable oils also show poor corrosion protection (Ohkawa et al., 1995). The presence of ester functionality renders these oils susceptible to hydrolytic breakdown (Rhodes et al., 1995). Therefore, contamination with water in the form of emulsion must be prevented at every stage. Low-temperature study has also shown that most vegetable oils undergo cloudiness, precipitation, poor flow, and solidification at -10°C upon long-term exposure to cold temperature (Rhee et al., 1995; Kassfeldt and Goran, 1997) in sharp contrast to mineral oil-based fluids.

In this study, we present a novel synthetic approach for chemical modification of vegetable oils to improve their thermo-oxidative and low-temperature stability. The structural modification is carried out in two stages, (i) synthesis of di-hydroxylated soybean oil from epoxidized soybean oil and (ii) reaction of anhydride with the di-hydroxylated product.

2. Experimental procedure

2.1. Synthesis of di-hydroxylated soybean oil from epoxidized soybean oil

Epoxidized soybean oil (ESBO) was obtained from Elf Atochem (Philadelphia, PA) and used without any further purification. Perchloric acid (HClO_4 , 70%) was obtained from Aldrich Chemical Company (Milwaukee, WI). The reaction was carried out in a three-neck, 5000 ml round bottom flask (Ace Glass Inc., Vineland, NJ). A 2450 ml aqueous solution of 127.4 g epoxidized soybean oil was refluxed for 48 h at 100°C in the presence of HClO_4 (26.05 g) added dropwise into the reaction vessel. A mechanical stirrer (Stir-pak^R,

Cole Parmer Instrument, Vernon Hills, IL) was used for continuous stirring of the reaction mixture. After the reaction was complete, the mixture was cooled to room temperature, and the organic phase extracted with chloroform (CHCl_3 , Fisher Scientific, Springfield, NJ) and washed three times with water to remove any traces of residual acid in the system. The solvent was removed under reduced pressure and the product stored overnight under dry vacuum.

2.2. Synthesis of di-hexanoyl-soybean oil from di-hydroxylated soybean oil

To 40 g of di-hydroxylated product (di-OH-SBO) prepared previously, 40 g of hexanoic anhydride (99%, Aldrich Chemical Company) was added in a 1:1 ratio, and to this mixture 19.97 g of pyridine (Aldrich Chemical Company) was added in equimolar ratio. The mixture was mechanically stirred in a 500 ml glass round bottom flask for 48 h at room temperature. The product mixture was then quenched with ice water and stirred for an additional 12 h, and later extracted several times with diethyl ether (Fisher Scientific, Springfield, NJ). The organic phase was washed with 100 ml 3% HCl and 5% NaHCO_3 (each three times) and finally dried over anhydrous MgSO_4 (Fisher Scientific, Springfield, NJ) for 24 h. Diethyl ether was removed under reduced pressure and the product stored under vacuum.

2.3. NMR analysis

All the ^1H and ^{13}C NMR spectra were recorded quantitatively using a Bruker ARX-400 spectrometer (Bruker, Rheinstetten, Germany) at a frequency of 400 and 100 MHz, respectively, using a 5 mm dual probe. For the ^1H and ^{13}C experiments, sample solutions were prepared in deuterated chloroform (CDCl_3 , 99.8% D, Aldrich Chemical Company) in 15 and 30% (v/v) concentrations, respectively. Proton NMR spectra were obtained from 16 co-added FIDs with a delay time of 1 s. For the distortionless enhancement by polarization transfer (DEPT 135) measurements, similar sample concentration as in ^{13}C experiment was used ($\text{NS} = 5000$, $\text{AQ} = 0.62$ s, $\text{DW} = 19\ \mu\text{s}$, $\text{D1} = 0.1$ s). This technique was useful to identify and compute the relative distribution of $-\text{CH}_n-$ ($n = 0-3$) carbons in the products.

2.4. FTIR analysis

Infrared spectra were recorded on a Perkin-Elmer spectrum RX FT-IR system (Beaconsfield, UK) equipped with a KBr beam splitter. A regular scanning range of $400\text{--}4000\text{ cm}^{-1}$ was used for 16 repeated scans at a spectral resolution of 4 cm^{-1} with a pair of KBr crystals. The spectra were recorded in transmittance mode.

2.5. Pressure differential scanning calorimetry (PDSC) method

The experiments were done using a DSC 2910 thermal analyzer from TA Instruments (New Castle, DE) attached to a computer. Typically, a 2.0 mg sample was taken in a hermetically sealed type aluminum pan with a pinhole lid for interaction of the sample with the reactant gas (dry air). A film thickness of less than 1 mm was required to ensure proper oil–air interaction and eliminate gas diffusion limitations. The module was temperature calibrated using the melting point of indium metal (156.6°C) at $10^\circ\text{C}/\text{min}$ heating rate. Dry air (Gateway Airgas, St. Louis, MO) was pressurized in the module at a constant pressure of 1379 kPa. A scanning rate of $10^\circ\text{C}/\text{min}$ was used during the length of the experiment. The start (T_S) and onset (T_O) temperatures of oxidation were calculated from the exotherm in each case.

2.6. Thin film micro-oxidation (TFMO) method

The test oil ($25\text{ }\mu\text{l}$) spread as a thin film on an activated high carbon steel catalyst surface was oxidized with a steady flow ($20\text{ cm}^3/\text{min}$) of dry air passing over the heated sample. Oxidation was carried out at a constant temperature (175°C) inside a bottomless glass reactor. A hot plate (MirakTM with built-in thermocouple controller by Thermolyne Inc., Dubuque, IA) was used to maintain the temperature within $\pm 1^\circ\text{C}$. A constant airflow ensured removal of volatile oxidation products as well as a steady concentration of air blanket on the oil film. After a specific time length, the catalyst with the oxidized oil sample was removed from the oxidation chamber and cooled rapidly under a steady flow of dry N_2 and immediately transferred to a desiccator. Later (approximately 1 h), the catalyst was weighed for sample loss due to thermal evaporation

(or gain due to oxidation) and soaked (30 min) with tetrahydrofuran (THF) to dissolve the soluble portion of oxidized oil. After dissolving the soluble oil portion, the catalyst containing the insoluble deposit was placed in desiccator for complete removal of any trace solvent and then weighed to determine the insoluble deposit.

2.7. Pour point and low-temperature stability method

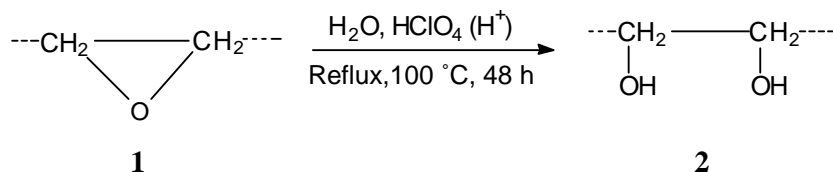
Pour points were measured by following the ASTM D97 (ASTM, 2000) method. A 50 ml sample was taken in a test jar and a thermometer (measuring from $+20$ to -80°C) was immersed into the sample. These test jars were placed in a digital pour point bath (Petrolab, NY). Temperature was measured in 3°C increments at the top of the sample until it stopped pouring. The pour point is defined as the temperature in $^\circ\text{C}$ when the sample still pours when the jar is tilted. Statistically, the method has shown quite good consistency for determining low-temperature flow property of fluids.

The same experimental setup (ASTM D 97) (ASTM method, 2000) was used for low-temperature stability measurements. The samples were kept at -25°C and visually inspected every 24 h for 7 days for fluidity (similar to pour point determination). Failing criteria consisted of crystallization, solidification and formation of solid particles, but did not include haziness and loss of transparency.

3. Results and discussion

Preparation of di-OHx-soybean oil (di-OHx-SBO) from ESBO via di-OH-SBO is an effective way of introducing branching on the fatty acid (FA) chain of vegetable oils. This reaction is carried out in two stages and the final product has significantly improved thermal, oxidative, and low-temperature stability compared with unmodified soybean oil (Scheme 1).

The removal of unsaturation in the soybean oil by converting them to epoxy-groups **1**, significantly improves the thermal and oxidative stability of the oil. It has already been established that the presence of multiple double bonds in the vegetable oil FA chains accelerates oxidative degradation (Adhvaryu and Erhan, 2002 and references therein). This is observed from



Scheme 1.

Table 1
Thin film microoxidation of the oils^a: 175 °C, 25 μl , 1 h

Test oils	Volatile loss (%)	Insoluble deposit (%)
SBO	12.17	65.85
1 , ESBO	7.02	9.53
3 , OAc-SBO	12.09	9.14
4 , Obu-SBO	28.02	15.07
5 , Ohx-SBO	57.83	28.33

SBO: soybean oil; ESBO: epoxidized soybean oil; OAc-SBO: acetoxo-SBO; Obu-SBO: butoxy-SBO; Ohx-SBO: hexanoyl-SBO.

^a Average of two independent experiments.

the TFMO and PDSC data in Tables 1 and 2. However, the low-temperature fluidity of **1** is poor and found to solidify at 0 °C (see Table 2). This would limit the application of vegetable oil at low operating temperature especially as automotive and industrial fluids.

The presence of one or two epoxy group per FA chain in the soybean oil (depending on the oleic and linoleic content) makes it highly susceptible to acid catalyzed ring opening in aqueous medium. A suitable approach to improve the low-temperature flow behavior of **1** is to attach branching sites at the epoxy car-

Table 2
Pour point^a and pressurized differential scanning calorimetry of the oils at 10 °C/min. Air at 1379 kPa constant pressure^b

Test oils	Start temperature (T_S) (°C)	Onset temperature (T_O) (°C)	Pour point (°C)
SBO	161.3	178.2	−6
1 , ESBO	177.4	203.9	0
3 , OAc-SBO	135.7	165.1	−3
4 , Obu-SBO	140.1	170.2	−3
5 , Ohx-SBO	171.9	196.6	−18

SBO: soybean oil; ESBO: epoxidized soybean oil; OAc-SBO: acetoxo-SBO; Obu-SBO: butoxy-SBO; Ohx-SBO: hexanoyl-SBO.

^a ASTM D 97.

^b T_S and T_O values are average of three independent experiments. Standard error = ± 1 °C.

bons. This was achieved by careful ring opening to obtain the di-hydroxy product **2**. An aqueous solution of **1** was refluxed for 48 h in the presence of an acid (perchloric acid, HClO_4). The acid has a tendency to hydrolyze the ester group, and thereby, destroy the triacylglycerol structure. The retention of the triacylglycerol backbone is very important to maintain excellent biodegradable character of vegetable oils. Care must be taken not to exceed the temperature above 100 °C to prevent molecular cleavage at the ester linkage. It was also observed that excess of water in the vessel allowed the reaction to go in the forward direction. The viscosity of **2** is substantially increased due to hydrogen bonding through $-\text{OH}$ pair than compound **1**.

FTIR spectra of dihydroxy compound **2** show well resolved peaks at 722, 755, 1099, 165, 1240, 1377, 1460, 1741, 2851, 2925 and 3431 cm^{-1} (Fig. 1). The absorption due to the epoxy group (822 and 842 cm^{-1}) in **1** is not observed in **2** and **5**. This fact suggests that **1** undergoes complete ring opening under the reaction condition. The consequent generation of free $-\text{OH}$ groups results in dimeric ($3550\text{--}3400\text{ cm}^{-1}$) and smaller amount of polymeric ($3400\text{--}3200\text{ cm}^{-1}$) association through H-bonding. Hydrogen bonds result in broadening of the $-\text{OH}$ absorption in the range ($3550\text{--}3200\text{ cm}^{-1}$), and these are readily broken on dilution. The presence of these intermolecular H-bond increases the viscosity of product **2**.

^1H nuclear magnetic resonance measurements on **1** indicate that the epoxy group is present in the δ 3.0–3.2 ppm region (Fig. 2). The methine proton of $-\text{CH}_2\text{---CH---CH}_2-$ backbone at δ 5.1–5.3 ppm, methylene proton of $-\text{CH}_2\text{---CH---CH}_2-$ backbone at δ 4.0–4.4 ppm, CH_2 proton adjacent to two epoxy group at δ 2.8–3.0 ppm, $-\text{CH}-$ protons of the epoxy ring at δ 3.0–3.2 ppm, $\alpha\text{---CH}_2$ to $>\text{C=O}$ at δ 2.2–2.4 ppm, $\alpha\text{---CH}_2$ to epoxy group at 1.7–1.9 ppm, $\beta\text{---CH}_2$ to $>\text{C=O}$ at δ 1.55–1.7 ppm, $\beta\text{---CH}_2$ to epoxy group at δ 1.4–1.55 ppm, saturated methylene groups δ

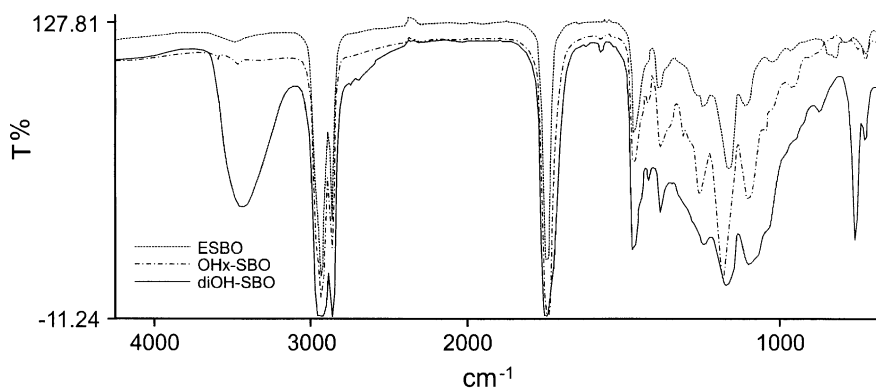


Fig. 1. Overlay FTIR spectra of epoxidized soybean oil **1**, dihydroxy compound **2**, and product **5**.

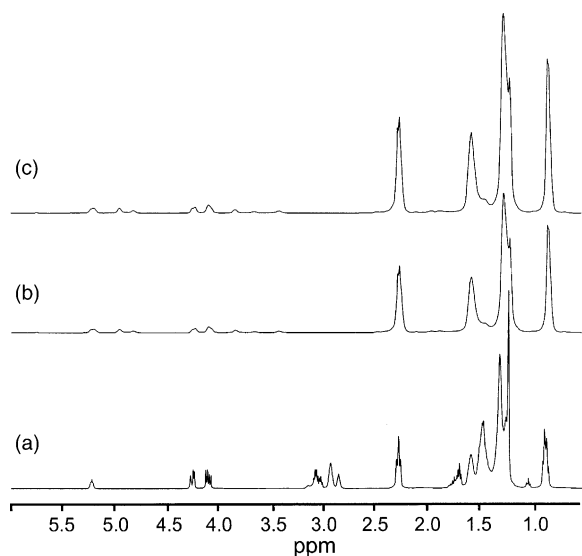


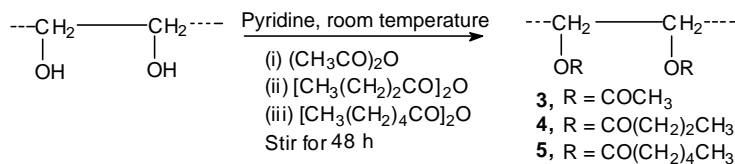
Fig. 2. Stacked ^1H NMR plot of: (a) epoxidized soybean oil **1**, (b) dihydroxy compound **2**, and (c) product OHx-SBO, **5**.

1.1–1.4 ppm and terminal $-\text{CH}_3$ groups at δ 0.8 – 1.0 ppm region. Compound **2** retains most of the characteristic peaks of compound **1** except the ones at δ 2.8–3.2 ppm and δ 1.4–1.55 ppm region, correspond-

ing to Hs attached to the epoxy groups and methylene groups adjacent to epoxy group, respectively.

The di-hydroxy compound **2** was then reacted with different anhydride in equi-molar ratio to obtain the corresponding products **3**, **4** and **5**. The reaction was carried out at room temperature under constant stirring of the mixture in equi-molar amount of pyridine for 48 h (Scheme 2).

The reaction mixture was then stirred with ice water for 12 h and the organic phase was extracted with diethyl ether. After successive washing and solvent removal, the products **3–5** were stored under vacuum. The TFMO data on these samples are presented in Table 1. It is observed that both volatile losses and insoluble deposits for **3–5** after oxidation in air at 175°C for 1 h are higher than **1**. The removal of unsaturation in SBO through epoxidation lowered volatile loss and deposit-forming tendency in **1**. However, the loss due to high-temperature volatility was found to increase steadily with an increase in carbon numbers of the attached pendent to epoxy carbons. Similar trend was observed during the PDSC experiments (see Table 2) where the addition of a branching site to the epoxy carbons resulted in a gradual increase in the start (T_s) and onset (T_o) temperatures of oxidation. T_o of compound



Scheme 2.

5 indicated an improvement in the high-temperature oxidative stability compared with SBO. The TFMO data suggested that the deposit forming tendencies might be problematic, however.

Microoxidation was carried out on SBO and products **1** and **5** for different time lengths. Fig. 3 presents the TFMO data on these samples at 175 °C with air. Epoxidation of $\text{C}=\text{C}$ bonds in SBO resulted in low insoluble deposit for 1 h during initial oxidation process. Thereafter, a sharp increase in the deposit formation suggests a catastrophic breakdown of the epoxy group leading to oxidative polymerization through the generation of reactive oxygen radicals. The addition of a side chain in **5** lowered the thermo oxidative stability of the oil, and deposit-forming tendency remained fairly low and constant over a period of time.

Fig. 2 illustrates the comparative study of the ^1H NMR spectra of **1**, **2** and **5** in CDCl_3 . It can be clearly seen from the stacked spectra that absorbance due to epoxy group is not present in the dihydroxy compound **2** and product **5**. The relative intensity of terminal methyl group (δ 0.8–1.0 ppm) is significantly higher in **5** than epoxy oil **1**. The absence of the peak at δ 1.4–1.55 ppm in **5** suggests that epoxy carbons of **1** are now the branching sites for side chains in compound **5**. The infrared spectra (Fig. 1) also illustrate that compound **5** do not show absorbance due to free or H-bonded OH groups. This explains the low viscosity of compound **5** when compared with **2**. It is also noticed that absorption due to epoxy group (822

and 842 cm^{-1}) no longer exists after hydroxylation **2** and in the final products **3–5**.

The low-temperature flow property of vegetable oils is extremely poor and this limits their use in sub-zero temperatures. Vegetable oils have a tendency to form macro crystalline structures at low temperature through uniform stacking of the ‘bend’ triacylglycerol backbone. Such macro crystals restrict the easy flow of the system due to loss of kinetic energy of individual molecules during self-stacking. SBO has a pour point of -6°C , whereas ESBO freezes at 0°C (see Table 2). The excellent thermal and oxidative stability of ESBO due to removal of unsaturation, however, results in poor cold flow property, and therefore limits its use in low-temperature applications. Attachment of a side chain with optimum length at the epoxy carbons improves the pour point significantly in **5** (-18°C). However, it was observed that short chains ($\text{C}_2\text{--C}_4$) did not make significant improvement in the cold flow behavior. It can be assumed that the presence of a side chain attached to the FA does not allow individual molecules to come close for easy stacking due to steric interactions. This results in the formation of microcrystalline structures rather than macro structures. At lower temperatures, such microcrystalline structures can easily tumble and glide over one another resulting in better fluidity of the total matrix.

4. Blending with additive and diluent

Further improvement in the low-temperature fluidity of compound **5** can be achieved by using suitable pour point depressant (PPD) additives. The PPD concentration was optimized by determining the pour point and low-temperature stability of several blends.

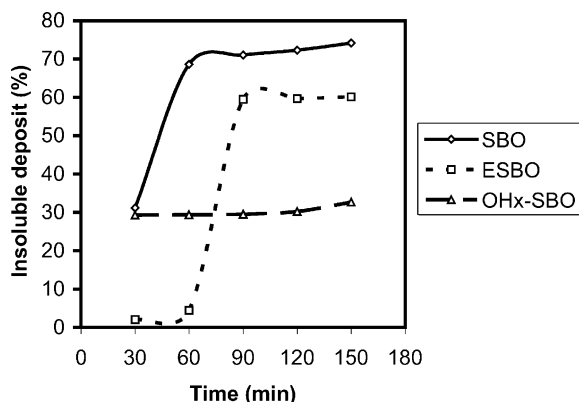


Fig. 3. Percent insoluble deposit of soybean oil (SBO), epoxidized soybean oil (ESBO, **1**) and product (OHx-SBO, **5**) during microoxidation at 175 °C, 1 h, air (flow rate 20 ml/min).

Table 3

Pour point^a of OHx-SBO after blending with additive and diluent

Test oil	PPD ^b (%)	Diluent ^c :oil (ratio)	Pour point (°C)
5 , OHx-SBO	0	0:100	−18
5 , OHx-SBO	1	0:100	−30
5 , OHx-SBO	1	30:70	−42

OHx-SBO: hexanoyl-SBO.

^a ASTM D 97.

^b PPD: pour point depressant.

^c Dibutyl adipate.

Table 4

Low-temperature storage stability test for OHx-SBO at -25°C for 7 days

Test oil	Observation
OHx-SBO + 1% PPD + diluent (70:30 oil:diluent ratio)	Pours at -25°C after 7 days; loss of transparency in the oil

The purpose of PPD is to hinder crystallization of triacylglycerol molecules at low temperature by further disrupting the stacking mechanism. An optimum PPD concentration of 1% in **5** was able to lower the pour point to -30°C (see Table 3). Further addition of PPD made no significant improvement in the pour point.

The addition of PPD alone was not sufficient to provide low-temperature storage stability for the chemically modified oil **5**. Product **5** in the presence of 1% PPD would freeze after 3 days at -25°C . In order to improve cold storage stability, a biodegradable synthetic ester, dibutyl adipate (96%, Aldrich Chemical Company) was added as a diluent with product **5**. Several concentrations of **5** and diluents were prepared through blending and cold storage stability was determined in each case (see Table 4). The optimized formulation containing chemically modified oil **5**, PPD, and an ester diluent had a pour point of -42°C and passed the 7 days storage stability test at -25°C (pour point of -36°C and 7 days of storage stability at -25°C is required for most industrial applications).

5. Conclusions

The process describes a systematic approach to modify chemically soybean oil to yield a base stock capable of operating at low temperature. The two-step method involving a dihydroxylated compound and the final branched product is described in detail. An optimum chain length of six carbons attached to the unsaturated carbon of the FA chain is able to demonstrate

excellent low-temperature flow and stability. Thermal and oxidative stability of the chemically modified oils were the best in product **5** (hexanoyl-SBO derivative) than in soybean oil. This fluid shows excellent low-temperature storage stability when blended with dibutyl adipate (in 70:30 ratio) and 1% additive, and is acceptable for most industrial applications.

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